

AD612492

LITHIUM-NICKEL HALIDE  
SECONDARY BATTERY INVESTIGATION

A. Lyall  
H. N. Seiger  
R. C. Shair  
Gulton Industries, Inc.

AD 612492

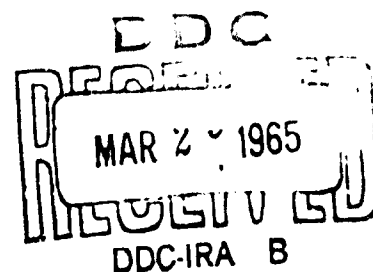
LITHIUM-NICKEL HALIDE  
SECONDARY BATTERY INVESTIGATION

A. Lyall  
H. N. Seiger  
R. C. Shair  
Gulton Industries, Inc.

TECHNICAL REPORT AFAPL-TR-65-11

JANUARY 1965

Air Force Aero Propulsion Laboratory  
Research and Technology Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio



## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Defense Documentation Center (DDC), Cameron Station, Alexandria, Virginia 22314.

This report has been released to the Clearinghouse for Federal Scientific and Technical Information, CFSTI (formerly OTS), Sills Building, 5285 Port Royal Road, Springfield, Virginia 22151.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security consideration, contractual obligations, or notice on a specific document.

## FOREWORD

This Final Technical Report was prepared by Gulton Industries, Inc., Metuchen, N. J. for the Research and Technology Division, Wright-Patterson Air Force Base, Ohio, under Contract No. AF 33(615)-1266, Project No. 8173, Task No. 817304. Mr. J. E. Cooper and Mr. W. S. Bishop were task engineers for the Air Force Aero Propulsion Laboratory. We wish to acknowledge the helpful discussions held with them.

The studies reported cover the complete contract period from December 1963 to December 1964.

## ABSTRACT

This report encompasses a study of the electrode processes, the electrolyte, and cell components of the nickel chloride-lithium cell. Some experimental work has been done on the nickel fluoride electrode, but excessive polarization voltages have restricted studies of this system.

Compatibility test results are discussed and recommendations for cell components made. Electrolytes, based on the compatibility tests, have been made and evaluated. A major modification to the propylene carbonate -  $\text{AlCl}_3$  electrolyte was made. The electrolyte is chlorinated and the excess chlorine scavenged with lithium metal. This modification has greatly reduced the kinetic polarization originally associated with the nickel chloride electrode.

A satisfactory lithium electrode has been prepared by pasting an oil mixture of powdered lithium, carbonyl nickel and a carboxymethylcellulose binder on an expanded nickel screen.

Three good separator materials have been found for the chloride system. Insufficient testing in the fluoride system has prevented endorsement as to their use in this case, although compatibility tests were affirmative.

Through the technique of "formation cycling", nickel chloride electrodes have been prepared which yield 80% utilization of the theoretical capacity. Concentration polarization at the nickel chloride electrode restricts the discharge rate to C/40 and charge rates to C/20. Methods of reducing the concentration polarization are outlined.

## PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE OF CONTENTS

	<u>PAGE NO.</u>
I. INTRODUCTION	1
II. COMPATIBILITY STUDIES	3
A. PROBLEM	3
B. METHOD OF SOLUTION	3
C. EXPERIMENTAL RESULTS	3
1. Materials of Construction	5
2. Separator Materials	6
3. Solvent-Solute Systems	6
a. Propylene Carbonate	6
b. Dimethylformamide	7
c. Nitrobenzene	7
d. N-Methyl-2-Pyrrolidone	8
e. Dimethylsulfoxide	8
III. ELECTROLYTE CONDUCTIVITY	12
A. PROBLEM	12
B. APPROACH TAKEN	12
C. EXPERIMENTAL RESULTS	12
IV. NEGATIVE (LITHIUM) ELECTRODE	16
A. PROBLEM	16
B. APPROACH TAKEN	17
C. EXPERIMENTAL RESULTS	17
V. POSITIVE (NICKEL HALIDE) ELECTRODES	20
A. PROBLEM	20

TABLE OF CONTENTS (Continued)

	<u>PAGE NO.</u>
B. APPROACH TAKEN	20
1. Nickel Chloride	20
2. Nickel Fluoride	23
3. Nickel Chloride Polarization	24
C. EXPERIMENTAL RESULTS	26
1. Preparation	26
2. Evaluation	26
3. Formation Cycling	38
4. Nickel Chloride-Magnesium Chloride Doped Electrodes	41
5. Nickel Fluoride	42
VI. ELECTROLYTE STUDIES	44
A. PROBLEM	44
B. METHOD OF APPROACH	44
C. EXPERIMENTAL RESULTS	44
1. Nitromethane-PCl <sub>5</sub>	44
2. Propylene Carbonate-AlCl <sub>3</sub>	45
VII. CONCLUSIONS AND RECOMMENDATIONS	48

LIST OF FIGURES, PLATES  
AND TABLES

	<u>PAGE NO.</u>
FIGURE 1.      Top -      CATHODE TABS AFTER 3 FORMATION CYCLES SHOWING CORROSION	19
Bottom - ANODE SUPPORT GRID AFTER REMOVING LITHIUM SHOWING EFFECT OF UNEVEN COATING BEFORE COMPRESSING PLATE	
FIGURE 2.      APPARATUS FOR CONCENTRATION POLARIZATION STUDIES	25
FIGURE 3.      WEIGHT GAIN OF NICKEL CHLORIDE Vs NUMBER OF IMPREGNATION CYCLES AT ROOM TEMPERATURE	27
FIGURE 4.      EXPERIMENTAL CELL CONFIGURATION	29
FIGURE 5.      NICKEL CHLORIDE-LITHIUM POLARIZATION TEST	30
FIGURE 6.      POSITIVE ELECTRODE DISCHARGE (Second Cycle)	32
FIGURE 7.      POLARIZATION TEST WITH CHLORINATED ELECTROLYTE	35
FIGURE 8.      FORMATION CYCLE #3 - PORTION OF CHARGE	40
FIGURE 9.      POLARIZATION STUDIES $\text{NiF}_2$ ELECTRODE ON CHARGE	43
TABLE I          SOME NON-AQUEOUS SOLVENTS	4
TABLE II        COMPATABILITY TEST RESULTS	9
TABLE III       ELECTROLYTE CONDUCTIVITY VALUES IN MILLIMHOS - $\text{Cm}^{-1}$ - CHLORIDE SYSTEM	14
TABLE IV        CONDUCTIVITY OF SOLVENT-SOLUTE COMBINATIONS TEMPERATURE $24^\circ\text{C}$ - FLUORIDE SYSTEM	15
TABLE V        BASE MATERIALS	17
TABLE VI        NICKEL CHLORIDE IMPREGNATING SOLUTIONS	26



## I INTRODUCTION

The goal of this project is to develop a secondary battery utilizing the electrochemical system of lithium and a nickel halide, specifically nickel chloride or nickel fluoride. The system should have a useable energy to weight ratio of 200 watt-hours per pound for the lithium-nickel chloride couple and 300 watt-hours per pound for the lithium-nickel fluoride couple. Because of the spontaneous oxidation of lithium in water and many other solvents, particularly those with an active hydrogen, selection of a suitable and compatible electrolyte is a major consideration. In order to achieve the energy to weight ratio goals at reasonable discharge rates, the electrolyte must have a conductivity of  $10^{-2}$  mhos  $\cdot$  cm $^{-1}$  or better. This is a resistivity of 100 ohms-cm. The resistivity of aqueous electrolytes is in the range of 5 to 10 ohms-cm. By setting a 10 to 20 times greater limit on the internal resistance of a cell, we establish a limit of  $10^{-2}$  mhos-cm $^{-1}$ . At the present time this lower limit has been obtained with propylene carbonate -  $\text{AlCl}_3$  -  $\text{LiCl}$  electrolyte.

This project, then, encompasses two systems; a lithium-nickel chloride system and a lithium-nickel fluoride system. Each system has its own advantages and disadvantages. The fluoride system is theoretically capable of a higher power to weight ratio than the chloride system. Also, lithium fluoride is less hydrophilic than lithium chloride. The problems of polarization and utilization of the nickel halide were found to be severe in the case of the fluoride. Electrolyte conductivity was also less in the fluoride system. Because there appeared to be a more favorable situation for achievement in the chloride system at this time, the major emphasis was eventually placed on this system.

Manuscript released by the authors March 5, 1965 for publication as an RTD Technical Report.

Best Available Copy

A good lithium electrode having satisfactory physical and electrochemical properties was achieved early in the program. Initially there were problems of adhesion of the discharged lithium halide on the grid and poor polarization characteristics on charge, but these were eliminated.

The positive electrode has been, and is still, the problem electrode. Two types of polarization have been found. The first is a function of the electrolyte-electrode couple, and can best be described as a catalytic or kinetic polarization. The second is a concentration polarization. Improvements in the electrolyte, through chlorination, have reduced the first type (catalytic or kinetic polarization). Concentration polarization is now the major factor restricting discharge rates.

## II COMPATABILITY STUDIES

### A. PROBLEM

With the great number of possible electrolytes in the non-aqueous field from which to choose, some limiting parameters were imposed, and then, within this restricted field, a series of tests were conducted.

The problem is to determine if the proposed materials are chemically and physically compatible. This is necessary to know before selecting the candidate materials for support grids of the electrodes, electrolyte, solvents and solutes, case materials, active materials (lithium, lithium halide, nickel and nickel halide) and separator materials.

### B. METHOD OF SOLUTION

The materials under consideration were placed together in sealed containers for a period of 30 days and examined for physical or chemical change. During this phase both the chloride and fluoride ions were evaluated.

### C. EXPERIMENTAL RESULTS

The first phase was to narrow the field of possible electrolyte solvents. Those considered are given in Table I. This was done by putting an arbitrary lower and upper region of boiling and freezing points so that work could be carried out at room temperature without elaborate equipment. Next solvents of low viscosity and high dielectric constants were sought. Many compounds were ruled out because of their known reactivity with lithium.

The next phase of the study was to determine if the proposed materials for the battery cell were compatible from a physical and chemical prospective. This was done with corrosion coupons placed in sealed test jars with the various solvent-solute combinations of electrolytes.

TABLE I.  
SOME NON-AQUEOUS SOLVENTS  
CONSIDERED FOR ELECTROLYTES

<u>SOLVENT</u>	<u>DIELECTRIC CONSTANT</u>	<u>BOILING POINT °C</u>	<u>MELTING POINT °C</u>	<u>VISCOSITY CPS</u>
Water (for reference)	80	100	0	1.000
H <sub>2</sub> SO <sub>4</sub>	110	330	10	25.4
HF	84	19	-83	0.24
Formamide	109	193	2	3.30
HCN	114	25	-13	0.201
Hydrazine	53	113.5	1.4	0.97
NH <sub>3</sub>	22	-33	-78	0.265
SeOCl <sub>2</sub>	46	176	11	
Formic Acid	58	101	8	1.804
Acetonitrile	36	81	-41	0.345
Propylene Carbonate	64	242	-49	2.53
Acetamide	59	222	81	
Glycol	38	197	(too high) -17	19.9
Furfural	46	162	-36	1.49
Nitrobenzene	35	211	5.7	2.03
Glycerol	42	290	17.0	9.54
Dimethyl Formamide		153	-61	---
Acetyl chloride- acetyl oxide		---	---	---
Acetyl chloride		52	-112	---
Bromine Trifluoride		128	9	---
N-methyl-2-pyrrolidone		202	-24	1.65
Dimethyl sulfoxide	49	189	18	1.98
Nitromethane		101	-29	0.620

In cases where there is no doubt of the compatibility of two materials, based on prior work, these were checked as a pair against a third to investigate interactions. A factorial designed experiment was established using Teflon FEP containers, since it is so inert.

Electrodes of lithium were prepared on an expanded nickel support material by dipping the support in molten lithium. These electrodes were weighed before and after their immersion in electrolyte to determine losses through dissolution or gain through interaction.

These proved to be unsuitable because of poor adhesion of the granular lithium surface to the nickel screen. Further compatibility testing was done by using a piece of pure lithium wire and nickel screen placed in the test container. This gave a good visual test of the lithium surface also.

The nickel chloride electrodes were prepared as outlined in Section V.

The samples were inspected visually after 48 hours at 30°C and then again after 96 hours. At the end of 7 days the samples were removed, washed in hexane, dried and weighed. They were returned to the solvent for another 23 days if there was no appreciable attack or reaction.

In the following tables are presented the apparent facts found in each case. These are set forth under the heading for each material.

#### 1. Materials of Construction

Silver, Monel 401, nickel 200 and nickel 201, Teflon, polyethylene and polypropylene have been found to be satisfactory in all solvent-solute systems tested. Type 304L stainless steel shows some attack at the interface if any free chlorine is present. In the case of silver in the presence of ammonium chloride and some amines with lithium chloride, there was a whitish surface coating which was not thick enough to weigh with an analytical balance ( $\pm 0.1$  mg). This may have been the result of a previously formed oxide film. This is usually found on silver.

## 2. Separator Materials

None of the separator materials tested were affected by the other candidate materials at room temperature. Nylon and dynel were not tested because of their known susceptibility to the solvents. The three satisfactory materials are a non-woven polypropylene, a Teflon fiberglass, and a fiberglass-asbestos material.

## 3. Solvent-Solute Systems

### a. Propylene Carbonate (PC)

Two types of tests were involved. The first was with PC as it came from the vendor, free from water and alcohol. The later series of tests were conducted with PC which was chlorinated after adding the solute, and then scavenged with lithium metal to remove excess chlorine.

When a lithium or ammonium chloride salt was added to unchlorinated PC, there was a discoloration of the lithium metal. In one case where a sample of polypropylene separator was included with the lithium chloride, there was a white coating formed on the surface. This was assumed to be LiOH formed as a result of moisture included in the lithium chloride, ammonium chloride and especially in the separator sample. All chlorides used were dried by reacting them with thionylchloride. The excess thionylchloride was removed by heating the material in a vacuum.



The separator material was stored in a desiccator with anhydrous  $\text{CaSO}_4$  for 24 hours prior to use or testing.

The chlorinated PC tests were similar. As long as all free chlorine was removed from the electrolyte prior to testing, results were similar.

b. Dimethylformamide (DMF)

When lithium wire was placed in the DMF, with or without nickel screening, it was noted that the surface was pitted after 48 hours, but very bright metallic in appearance. The solution was clear. After 96 hours the DMF showed signs of polymerization, but the lithium remained the same. After 7 days the DMF was almost a gel, but the lithium had lost 0.2% by weight and remained shiny though somewhat pitted.

The addition of ammonium chloride produced a reddish brown color as well as the previously described phenomena. The weight loss was also 0.2%.

c. Nitrobenzene (NB)

The nitrobenzene first formed a yellow surface on the lithium. During this process the NB became lighter in color. After a week in contact with lithium the NB was filtered and divided into two lots. In one was placed enough ammonium chloride to saturate it. In both were placed pieces of lithium wire and Ni screen--in the other was placed a piece of polypropylene separator. After 48 hours the cut ends of the wire in both lots showed discoloration becoming dark gray. After 96 hours the entire wire had the same dark gray color but no further action took place. There was no weight change after 7 days. At the end of 30 days the lithium wire again had a

slight yellow surface and a weight gain of 0.1% in both cases. A third sample which had been treated with lithium and filtered was used with lithium and a nickel chloride electrode.

When the lithium wire was removed, washed with hexane and dried, the yellow color became more pronounced. One piece was left in the air in order to determine reactivity in the nitriding reaction. The other piece was added to water to form the hydroxide. Both normally rapid reactions were extremely slow until the surfaces were scratched. The NB seems to have produced a protective coating on the lithium.

d. N-Methyl-2-Pyrrolidone (MP)

This solvent dissolved  $\text{NiCl}_2$  but not  $\text{NiF}_2$ . There seemed to be no reaction with lithium or separators.

e. Dimethylsulfoxide (DMSO)

The solvent also dissolved  $\text{NiCl}_2$  but not  $\text{NiF}_2$ . Lithium and lithium halide salts are not affected. The three separators were also satisfactory.

A summary of the compatibility tests is given in Table II.



TABLE II  
COMPATABILITY TEST RESULTS

NAR = No apparent reaction

PROPYLENE CARBONATE

<u>SOLUTE</u>	<u>ACTIVE MATERIAL</u>	<u>SEPARATOR</u>	<u>REMARKS</u>
None	Li/Ni	None	NAR
		Polypropylene	NAR
		Teflon- Fiberglass	NAR
		Dynel	NAR
		PVC	NAR
LiCl	Li/Ni	None	Weight gain (30%) possibly LiOH
LiCl (treated with SOCl <sub>2</sub> )	Li/Ni	None	NAR
LiF	Li/Ni	Polypropylene	NAR
NaF	Li/Ni	None	Lithium disintegrates to white powder.
LiCl	NiCl <sub>2</sub> · x H <sub>2</sub> O	None	NAR
LiF	NiF <sub>2</sub> · xH <sub>2</sub> O	None	NAR
NH <sub>4</sub> Cl	Li	None	Slight white deposition on Li surface.
AlCl <sub>3</sub>	Li	Asbestos- Fiberglass	NAR
LiCl/AlCl <sub>3</sub> /Cl <sub>2</sub>	Li/Ni/NiCl <sub>2</sub>	Polypropylene	NAR
PCl <sub>5</sub>	Li/Ni/NiCl <sub>2</sub>	None	NAR
NH <sub>4</sub> F	Li/Ni	None	NAR
KF	Li/Ni/NiF <sub>2</sub>	None	NAR
RbF	Li/Ni	None	NAR
ZnF <sub>2</sub>	Li/Ni	Polypropylene	NAR

NITROBENZENE

<u>SOLUTE</u>	<u>ACTIVE MATERIAL</u>	<u>SEPARATOR</u>	<u>REMARKS</u>
None	Li/Ni	Polypropylene	Some discoloration of Li surface. Weight gain 0.1%
LiCl	Li/Ni/NiCl <sub>2</sub>	Teflon-Fiberglass	Same as Li alone but less gain.
NH <sub>4</sub> Cl	Li	None	Slight discoloration

HYDRAZINE

None	Li/Ni	None	NAR for 96 hours. At 7 days plate was dissolving. Only white powder remained on Ni screen.
------	-------	------	--

ETHYLENE GLYCOL

None	Li/Ni	None	NAR for 48 hours but 96 hours showed degradation. At 7 days all Li had dissolved.
------	-------	------	---

FORMAMIDE

None	Li/Ni	None	Vigorous reaction immediately. Evolution of gas.
------	-------	------	--

ACETONITRILE

None	Li/Ni	Polypropylene	Reaction with lithium after 48 hours. Test for water positive.
None	Li/Ni	Polypropylene	NAR with new dried solvent at 7 days. Slowly deteriorated during 30 day stand. Dissolved Li.

DIMETHYLFORMAMIDE

<u>SOLUTE</u>	<u>ACTIVE MATERIAL</u>	<u>SEPARATOR</u>	<u>REMARKS</u>
None	Li	None	Polymerization of DMF and dissolution of Li - white polymer.
LiCl	Li/Ni	Polypropylene	Same as Li alone. No effect on separator.
NH <sub>4</sub> Cl	Li	None	Same as above but solution brown.

N-Methyl-2-pyrrolidone

LiCl	Li/Ni/NiCl <sub>2</sub>	None	NiCl <sub>2</sub> dissolves
LiCl	Li/Ni	None	NAR
NH <sub>4</sub> F	Li/Ni	None	NAR
LiF	Li/Ni	None	NAR
ZnF <sub>2</sub>	Li/Ni/NiF <sub>2</sub>	Polypropylene	NAR

DIMETHYLSULFOXIDE

LiCl	Li/Ni/NiCl <sub>2</sub>	None	NiCl <sub>2</sub> dissolves
LiCl <sub>2</sub>	Li/Ni	None	NAR
RbF	Li/Ni/NiF <sub>2</sub>	Polypropylene	NAR
ZnF <sub>2</sub>	Li/Ni/NiF <sub>2</sub>	None	NAR

### III. ELECTROLYTE CONDUCTIVITY

#### A. PROBLEM

Although there has been a considerable amount of work done in the field of nonaqueous solvent chemistry, there has been very little on the electrochemical conductivity. The criterion of a high dielectric constant has not always been applicable, and ionization and conductivity have to be determined experimentally. The proposed electrolyte combinations first had to be screened for compatibility with the active materials of Li, LiCl, LiF, Ni, NiCl<sub>2</sub>, and NiF<sub>2</sub>. Unless the conductivity of the electrolyte is greater than 10 millimhos  $\text{-cm}^{-1}$  the internal resistance of a cell will be too great to allow a reasonable current drain during discharge and will result in charge voltages which could cause a breakdown in the electrolyte.

#### B. APPROACH TAKEN

Conductivity measurements were made on proposed electrolytes with a Freas conductivity cell. It has a cell constant of 1.0. Measurements were done using a 1000 cps signal generator and a Z-Y Bridge. An oscilloscope was used as a detector. The test cell was kept in an oil bath at 25°C. All results have been expressed in millimhos per cm.

#### C. EXPERIMENTAL RESULTS

The results of these tests are shown in Tables II and III. The first table is concerned with the chloride system and the second with the fluoride system.

The most satisfactory electrolyte for the chloride system to date is a propylene carbonate solution. This solution is 0.75M AlCl<sub>3</sub> saturated with chlorine gas at room temperature. The excess chlorine is scavenged with lithium metal. The solution is finally saturated with dry lithium chloride. The best electrolytes for the fluoride system to date are

N-methyl-2-pyrrolidone and dimethyl-sulfoxide, each saturated with zinc fluoride. These two solvents were not used with the chloride system because they dissolve nickel chloride. The solubility of nickel fluoride in these solvents is low enough to permit their use as a solvent for the fluoride electrolyte. However, the value of conductivity of the propylene carbonate -  $\text{AlCl}_3$  electrolyte and the nitromethane -  $\text{AlCl}_3$  electrolyte have been found to be one or two orders of magnitude greater than the best fluoride system to date.

TABLE III

ELECTROLYTE CONDUCTIVITY  
VALUES IN MILLIMHOS -  $\text{Cm}^{-1}$   
CHLORIDE SYSTEM  
TEMPERATURE  $25^{\circ}\text{C}$

SOLVENT	SOLUTE	SOLUTION CONCENTRATION	CONDUCTIVITY
Propylene Carbonate	Li Cl	Saturated	.584
Propylene Carbonate	Al Cl <sub>3</sub>	0.75M	16.7
Propylene Carbonate	AlCl <sub>3</sub> + LiCl	0.75M and Saturated	9.53
Propylene Carbonate	Ca Cl <sub>2</sub>	Saturated	.066
Propylene Carbonate	KCl	Saturated	.038
Propylene Carbonate	NH <sub>4</sub> Cl	Saturated	.020
Propylene Carbonate	Na Cl	Saturated	.010
Propylene Carbonate	Ba Cl <sub>2</sub>	Saturated	.068
Propylene Carbonate	P Cl <sub>5</sub>	23.5 g/L	12.5
Nitromethane	Li Cl	Saturated	.001
Nitromethane	NH <sub>4</sub> Cl	Saturated	.001
Nitromethane	Al Cl <sub>3</sub>	Saturated	3.26
Nitromethane	Li Cl	Saturated	.010
Nitromethane	AlCl <sub>3</sub> + LiCl	Both Saturated	35.7
Nitromethane	P Cl <sub>5</sub>	13.3 g/L	20.0
Propylene Carbonate	AlCl <sub>3</sub> + LiCl <sub>2</sub> chlorinated	Saturated with LiCl Excess Cl <sub>2</sub> removed with Li Metal	13.8
Nitrobenzene	LiCl	Saturated	$\sim 1 \times 10^{-3}$
Nitrobenzene	NH <sub>4</sub> Cl	Saturated	$\sim 1 \times 10^{-3}$
Nitrobenzene	AlCl <sub>3</sub>	Saturated	3.26

TABLE IV

CONDUCTIVITY OF SOLVENT-SOLUTE COMBINATIONS  
TEMPERATURE 24°C

## FLUORIDE SYSTEMS

	$\text{NH}_4\text{F}$	$\text{LiF}$	$\text{NaF}$	$\text{KF}$	$\text{RbF}$	$\text{MgF}_2$	$\text{CaF}_2$	$\text{BaF}_2$	$\text{ZnF}_2$	$\text{PbF}_2$	$\text{AlF}_3$
Propylene Carbonate	.008	.008	.008	.013	.030	.005	.510	.003	.095	.004	.002
Nitro-Methane	.011	.008	.003	.028	.184	.002		.007	.052	.005	.003
Dimethyl Sulfoxide	.288	.005	.003	.390	.480	.007		.008	.850	.008	.018
Methyl Pyridone	.012	.008	.005	.049	.075	.002		.002	.900	.003	.003
Nitro Benzene	.002	.002	.001	.001	.008	.001		.002	.002	.003	.0005
P.C. Sat. with LiF									.011		
N. M. Sat. with LiF					.110				.005		
D.M.S. Sat. with LiF					.415				.264		
M.P. Sat. with LiF					.095				.603		

#### IV    NEGATIVE (LITHIUM) ELECTRODE

##### A. PROBLEM

There were three principal problems in producing a satisfactory lithium electrode. The first is to secure a good adhesion of the lithium and lithium salt to the support material. The second is a high utilization of theoretical capacity. The third is to obtain a low polarization during discharge and charge.

##### B. APPROACH TAKEN

Initially, electrodes were prepared by dipping an expanded nickel grid in molten lithium metal (in an inert atmosphere of dry argon). Electrodes produced in this manner had poor adhesion of the lithium and uneven surfaces. Control of the amount picked up was also poor.

The next approach was to make an electrode of a paste of powdered lithium in oil. This paste is a 30% dispersion of lithium in mineral oil. The particle size is  $< 20$  microns according to the manufacturer's specifications. The adhesion of the lithium, as such, on the nickel grid base was no problem, although the ratio of open grid area to solid support was somewhat critical. Experience in making pasted electrodes improved uniformity. The problem that developed was one of adhesion of the product formed on discharge (lithium chloride or fluoride, as the case may be).

A binder of carboxymethylcellulose (CMC), which was soluble in DMSO but not in propylene carbonate, was obtained. By adding 2% binder to the electrodes, the lithium chloride (discharged state) adhered to the grid.

The third problem, that of utilization, did not seem difficult. However, charge polarization was excessive. This was solved by incorporating a conductive diluent of carbonyl nickel powder to the lithium.



### C. EXPERIMENTAL RESULTS

Several types of nickel base material have been tried for the pasted electrodes. The degree of adhesion seemed to be dependent on the amount of base material available for the lithium to stick to. Perforated metal of 225 holes per square inch of .045 inches in diameter has been found unacceptable. An expanded metal mesh of 5/0 size has proven satisfactory as well as a 60 mesh wire cloth. These have a sufficient material to area ratio to support the lithium until it can be compressed at a pressure of 2 tons/in<sup>2</sup>, through which it gains mechanical strength.

TABLE V

#### SATISFACTORY BASE MATERIALS

	<u>METAL SURFACE</u>	<u>OPEN AREA</u>
PERFORATED METAL SHEET (with binder)	64.3	35.7
60 MESH SCREEN (007 wire)	66.1	33.9
EXPANDED METAL (5 Ni 9 - 5/0)	66.7	33.3

#### UNSATISFACTORY BASE MATERIALS

35 MESH SCREEN (.007 wire)	42.8	57.2
EXPANDED METAL (5 Ni 7 - 4/0)	35.0	65.0

The carbonyl nickel powder is < 10 microns. Using a 10 mole percent nickel admixture gives an electrode coating containing 50.6% lithium, 47.4% nickel, and 2% binder. A 10% solution of CMC in dimethylsulfoxide was added to the lithium-nickel oil dispersion so as to leave about 2% CMC in the pasted material after drying.

The materials are weighed out. The lithium-oil dispersion is placed in a weighing bottle in the glove box. Based on this weight, the weight of the nickel and binder are calculated. The binder is dissolved in DMSO. All ingredients are returned to the glove box when they are mixed. The lithium-nickel mixture is applied with a spatula to a base. Although this is done in a glove box under argon, it can be handled in the atmosphere as long as there is oil on the lithium surface. After a uniform layer of mix has been applied, the electrode is removed from the glove box, placed between two plates of polyethylene, and compressed at 2 tons per square inch. The electrodes are placed in a small glass vacuum chamber heated with resistance heating tapes.

The electrodes are vacuum dried since the dimethylsulfoxide boils at approximately  $190^{\circ}\text{C}$  which would soften the lithium particles and cause sintering. The electrodes are heated to  $90\text{--}100^{\circ}\text{C}$  under  $<2$  psia pressure for 15 minutes and then cooled. After the cooling, the vacuum chamber is placed in dry box where it is opened, under argon, and the electrodes washed with hexane to remove any residual mineral oil.

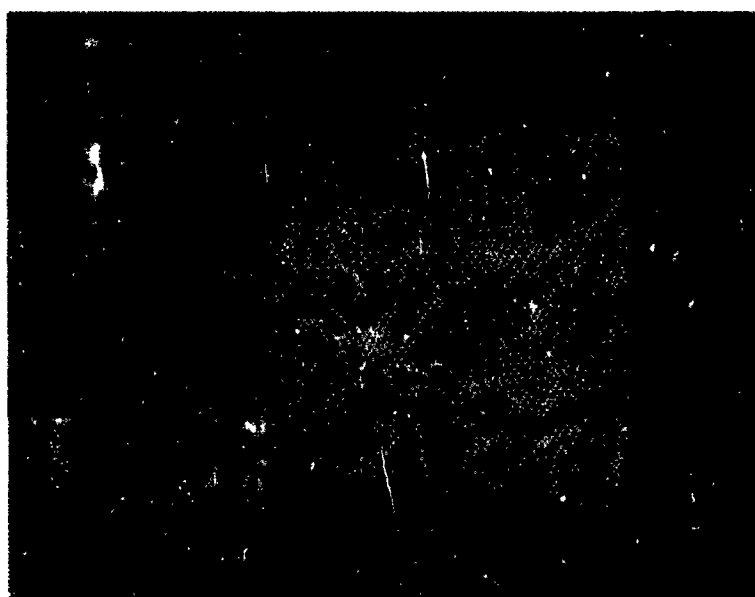
The lower photograph in Fig. 1. shows the expanded nickel screen from a lithium anode. The earlier coatings of lithium-nickel powder and CMC binder were uneven. When the plate was compressed, certain areas received excessive pressure, shearing the screen. This has been overcome by forming an epoxy edge bead coated to an even thickness. This also helps to control the amount of lithium deposited overall. The edge coat is applied before pasting and cured at  $150^{\circ}\text{C}$ . The thickness can be controlled by applying successive thin layers and curing each.

This edge coating also permits easier insertion of the anode into the polypropylene separator bag. It will also reduce any tendency for lithium to flake off at the edge.

FIGURE 1



CATHODE TABS AFTER 3 FORMATION CYCLES SHOWING  
CORROSION



ANODE SUPPORT GRID AFTER REMOVING LITHIUM SHOW-  
ING EFFECT OF UNEVEN COATING BEFORE COMPRESSING  
THE PLATE

## V POSITIVE (NICKEL HALIDE) ELECTRODES

### A. PROBLEM

In a generalization of the nickel halide-lithium system, the active material of the positive electrode during discharge is  $\text{NiX}_2$ . The discharge reaction may be represented by:



The mechanics of this requires a conductive material in close proximity to the nickel halide, since the latter is a semiconductor and not a conductor itself. The nickel halide is dispersed in the conductive material.

In a system using lithium, it is necessary to exclude any water. Moreover, because of the hydrophilic nature of nickel chloride, it is necessary to take extra measures in producing an anhydrous nickel chloride electrode. The nickel fluoride also is subject to moisture problems, but to a lesser degree.

Polarization was found to be the main problem with the positive electrode. Although some experiments were performed with the nickel fluoride electrode, the major emphasis was on the nickel chloride electrode. Both systems seem to suffer from the same problems of poor utilization and high polarization potentials. However, the problems are more acute with the fluoride system.

### B. APPROACH TAKEN

#### 1. Nickel Chloride

A sintered nickel plaque on a perforated nickel sheet base was used as the conductive matrix. This plaque is the same as is used for the cadmium electrode of the nickel-cadmium cell. A carbonyl nickel slurry

is sintered on a 3 mil thick perforated base. The base has 225 holes per square inch of .045 inches in diameter. The porosity of the sinter in the plaque is about 80% and the overall thickness is about 30 mils. The nickel chloride is introduced as a saturated solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in methanol. This solvent was used because of its low surface tension which facilitates the penetration of the solution into the pores of the nickel matrix. The plaques are placed in the solution in a beaker. The beaker is put in a bell jar and a vacuum of 27 inches pulled. After 5 minutes, the pressure is returned to atmospheric and the plates removed. The excess solution is wiped off with a glass doctor knife.

The plates are air dried at room temperature to remove all surface wetting. They are further dried at  $75^\circ$  to  $80^\circ\text{C}$  under 20 inches of vacuum for 2 hours. The vacuum jar in which the plates are dried is placed in the oven at room temperature, allowing the temperature to come up over a period of several minutes. The temperature is kept low to prevent creeping of the nickel chloride to the surface during drying. If the pressure is reduced below 20 inches of vacuum, the plates weep, even at room temperature, and a large percentage of the nickel chloride migrates to the surface of the plate.

The process is continued until a constant weight is obtained or the increase in weight after a cycle is negligible. The plates are then dried for 16 hours while the temperature is increased to  $130^\circ\text{C}$  and the pressure kept at 20 inches of vacuum. At this point a greater vacuum could be used, but it is kept constant for simplicity.

While still in the vacuum jar, the plates are cooled to room temperature. The jar and plates are transferred to a glove box having a dry atmosphere and the plates removed. They are stored in a desiccator over calcium sulfate until needed.

Half-cell experiments with these plates showed that as the positive electrode was discharged, the polarization decreased. Subsequent discharges on an electrode always showed less polarization than initially encountered. A cathode was made by electrochemically forming nickel chloride from nickel. This electrode showed less polarization than an electrode prepared by impregnating a plaque with nickel chloride crystals. These facts led to the suggestion that a formation cycle (discharging and recharging the cathode against a counter electrode before the assembly of the cell) should improve the initial polarization (current-voltage relationship). However, the utilization of the theoretical capacity does not improve sufficiently.

Two approaches were taken to increase the utilization of material. The first was to impregnate the sintered nickel plaque only once. This resulted in a cathode of 0.057 ampere hours per square inch. The polarization was markedly improved and the utilization was over 35%. A subsequent discharge yielded a 70% utilization. This again pointed to the advantage of a formation cycle. The next step was to make a cathode with two impregnation cycles and a formation cycle between. After the first impregnation, the cathode was discharged at a low current density. It was removed from this cell, washed to eliminate the residual electrolyte, dried, and reimpregnated. It was put back in the cell, charged, removed again, and rewashed to remove the electrolyte and dried. This cathode was assembled into a test cell fitted with a reference electrode and discharged against two lithium anodes.

The second approach taken to increase utilization of active material was to put lattice imperfections into the nickel chloride crystals through doping. The data on this phase is presented in section C.4.. This is hypothesized to improve the conductivity of the nickel chloride film on the sintered nickel substrate, and thus improve the utilization. To explain this, we quote

from an article by F. V. Schossberger.<sup>1</sup>

"In ionic crystals, electrons are transferred from one type of atom to another. At elevated temperatures, they exhibit ionic conductivity, and the existence of positive and negative ions causes strong optical absorption in the infrared region of the spectrum. Conduction in ionic crystals is usually associated with lattice defects. In ideal crystals, without defects, there would be no ionic conduction because all the ions would be held firmly in position in the lattice. Large electrical fields would be required to dislodge them. However, perfect crystals do not exist."....

"Frenkel relates the experimental data on ionic conduction to the presence of interstitial ions. His theory assumes that a small fraction of the ions leave their normal lattice sites and are present in interstitial positions. The movement of the interstitial ions and the vacancies are responsible for the observed rate of migration of ions in the electric field. This picture of lattice disorder was extended by Schottky and Wagner. They suggested that vacancies can occur in the crystal lattice if the missing ions are located on the surface. These two defects enable the stoichiometric composition and the electrical neutrality as a whole to be preserved."

To cause such lattice defects, 5% magnesium or stannous chloride (based on the  $\text{NiCl}_2$ ) was added to the impregnating solution.

## 2. Nickel Fluoride

The nickel fluoride electrodes were prepared by reacting a nickel hydroxide impregnated plaque with hydrofluoric acid. The nickel hydroxide plaque was a positive electrode from a nickel-cadmium cell. Prior to electrochemical formation, the nickel is in the form of  $\text{Ni}(\text{OH})_2$ . Aqueous HF was added dropwise to the plaques to react with the  $\text{Ni}(\text{OH})_2$ . The rate was controlled to evaporate the water before any drops appeared on the surface. A slight excess of acid (based on the stoichiometry of  $\text{Ni}(\text{OH})_2$  present) was

1 F. V. Schossberger, "Solid State Chemistry Gives Insight Into Crystal Behavior, Chem. Eng., Nov. 13, 1961, P. 231

added. The electrode was air dried at  $110^{\circ}\text{C}$  and then vacuum dried at the same temperature to a constant weight.

Both the polarization characteristics and utilization were determined in half cell studies. A nickel fluoride electrode of known theoretical capacity was discharged against a pair of counter electrodes. Potentials were read between the positive electrode and a reference electrode while the current was varied. When the positive electrode was exhausted, the polarity was reversed and the electrodes charged, again at varying currents.

For this test, a pair of lithium electrodes (without binder) were used as counter electrodes. The electrolyte was zinc fluoride dissolved in N-methyl-2-pyrrolidone. The reference electrode was magnesium coated with magnesium fluoride. The test cell was polyethylene and all work was conducted in a glove box in an argon atmosphere.

### 3. Nickel Chloride Polarization

When the polarization problems of the  $\text{NiF}_2$  electrode were found to be more severe than the  $\text{NiCl}_2$ , the major emphasis was placed on solving the problems of the chloride system. Studies were conducted to ascertain whether the polarization of the cathode is a concentration or a catalytic type. Normally, concentration polarization can be determined by the effect of agitating the electrolyte. However, with a sintered matrix, the surface agitation of the electrolyte would have little effect on the polarization taking place in the pores of the material.

The investigation of polarization with pores requires special apparatus. To study this, the electrolyte has to be pulled or pushed through the pores while current is being passed. For this kind of experiment, the apparatus shown in Fig. 2 was constructed. It consisted of a Buchner funnel and a filter flask. The electrodes, separators, and gaskets were placed as shown in this figure. A perforated disk of 1/8 inch polyethylene was placed



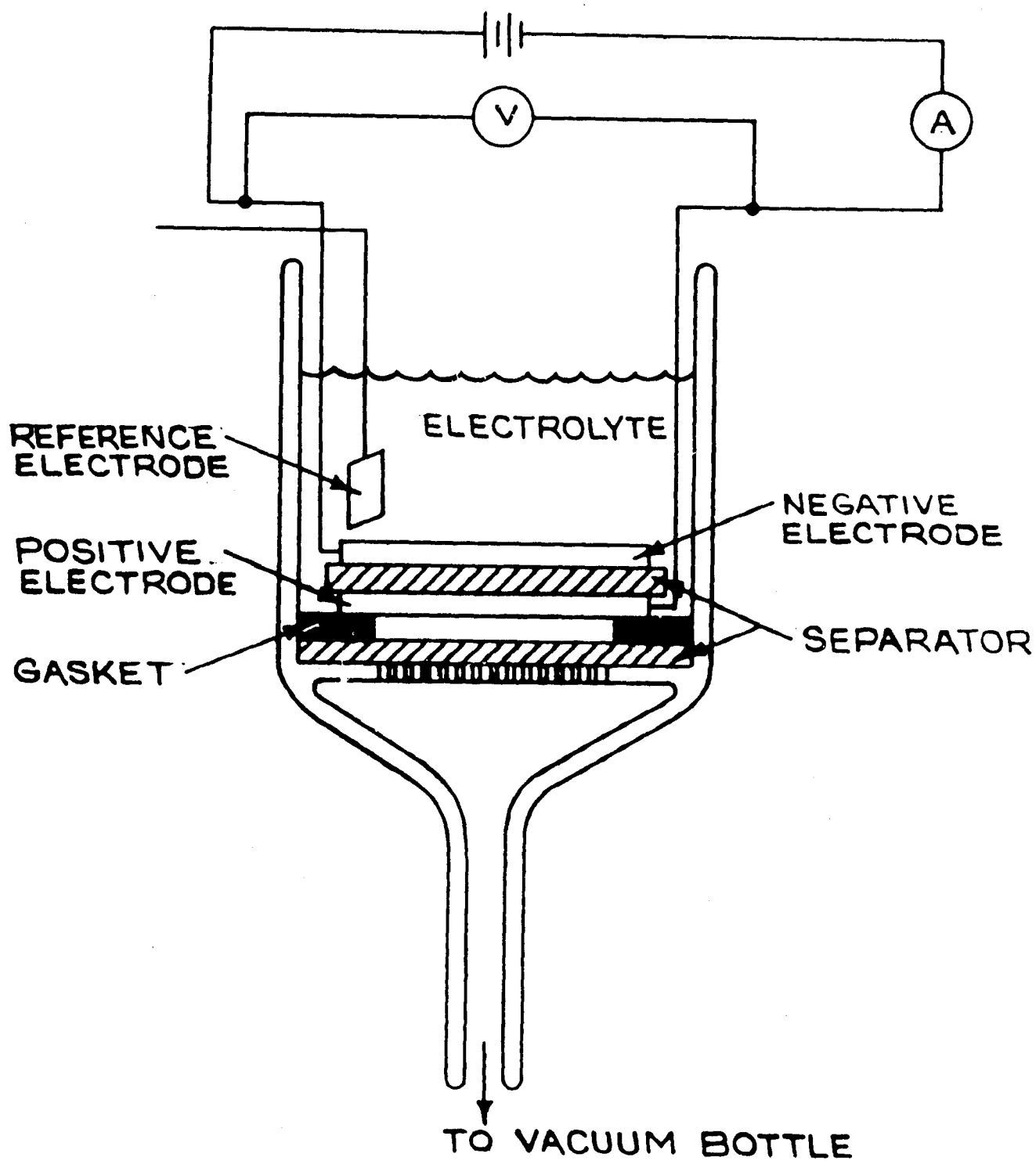


FIG. 2 APPARATUS *for* CONCENTRATION POLARIZATION STUDIES

over the negative electrode and held down with a glass rod in a clamp to give a tight packing of the electrodes. The negative electrode was a standard lithium pasted anode. The reference electrode was a mercury-mercurous chloride electrode.

### C. EXPERIMENTAL RESULTS

#### 1. Preparation

In the impregnation of nickel chloride electrodes, the average weight gain of anhydrous  $\text{NiCl}_2$  was 0.14 grams per square inch per cycle for the first four cycles. After that, each cycle achieves about 1/2 to 1/3 the pick-up of the previous cycle. The total pick-up averages 0.7 grams per square inch. This latter value is equivalent to 0.29 ampere hours

The average weight of the 30 mil thick blank plaques (exclusive of tab weight) is 0.92 grams per square inch. This gives an ampere hour per gram ratio of 0.179.

Figure 3 is a graph of the average pick-up of nickel chloride in grams per square inch versus impregnation cycle. This is for a 30 mil thick sintered nickel plaque of 80% porosity and without formation cycles.

The nickel chloride-methanol solution used had the following properties:

TABLE VI

$\text{Ni Cl}_2$	330 g/L
Density 20°C	1.1120
Viscosity 25°C	30 c.p.

#### 2. Evaluation

It was necessary to evaluate the electrodes to determine whether they are satisfactory for use in a cell. In the first of these tests, polarization studies were the primary objective. Capacities needed only be great

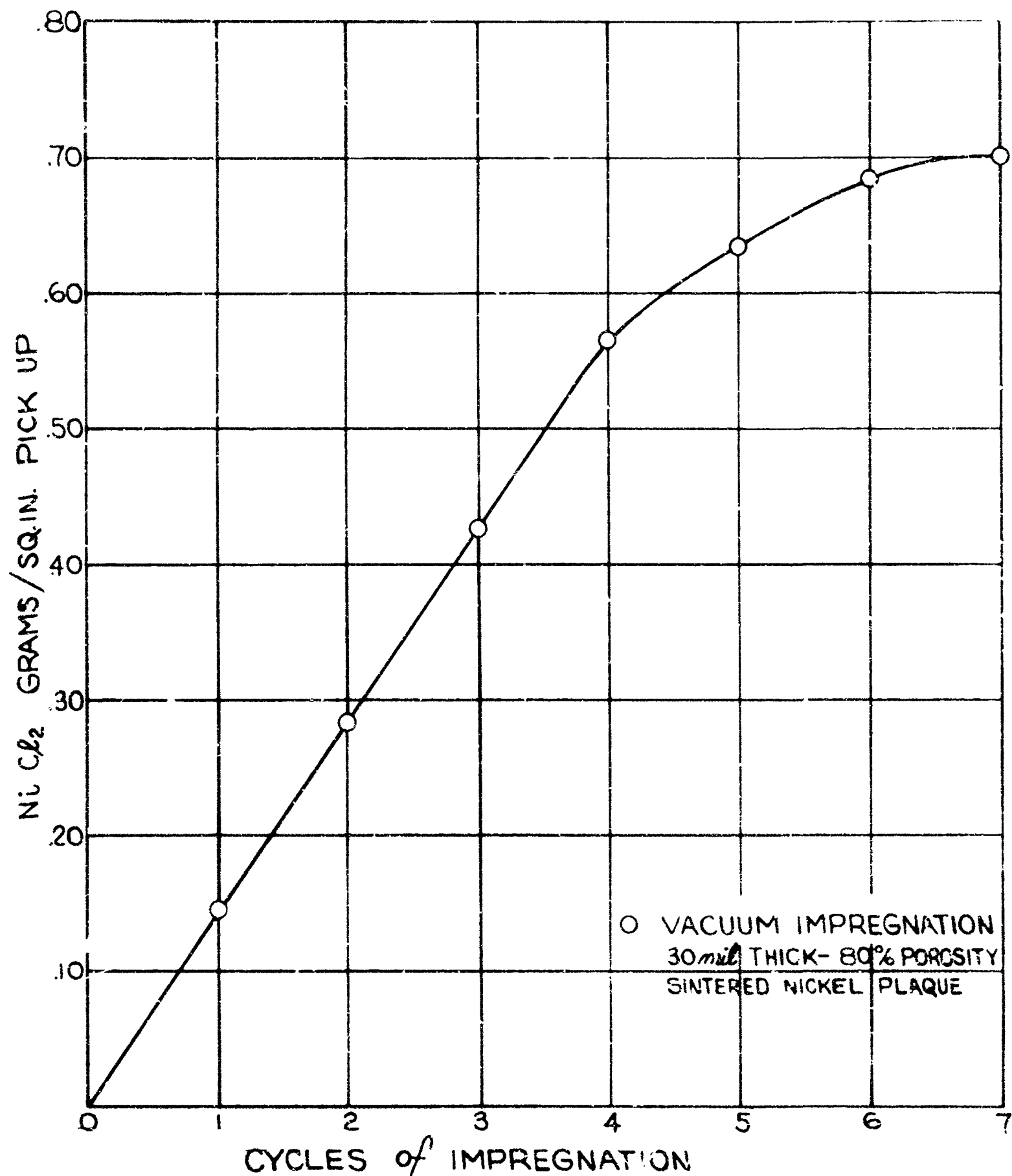


FIG. 3 WEIGHT GAIN of NICKEL CHLORIDE  
Vs NUMBER of IMPREGNATION  
CYCLES AT ROOM TEMPERATURE

enough to cause no complications in polarization data during discharge.

Using a case made of stainless steel and shims of polyethylene, an experimental cell was constructed of two pasted lithium electrodes and one positive ( $\text{NiCl}_2$ ) electrode, as shown in Figure 4. Two lithium electrodes were used, one with and one without nickel powder.

The nickel chloride electrode was bagged in a polypropylene separator and placed between the two negative electrodes. A reference electrode of mercurous chloride-mercury was used. All work was done in a dry box. The electrolyte of propylene carbonate -  $\text{AlCl}_3$  saturated with lithium chloride was used.

The current was varied up and down while voltage readings were taken between the reference electrode and the positive and negative electrodes. The cell was recharged at a low rate and a second discharge made at two current levels.

Electrochemical testing of the nickel chloride electrode indicated a very poor utilization factor and high polarization on discharge and charge, Figure 5. It was noted on the second discharge that the polarization was decreased slightly. This is not uncommon in a secondary system.

A technique used to overcome this problem is called "formation" when the electrodes are cycled against an accessory electrode prior to assembly in cells. This was tried using a ferrous-ferric chloride negative electrode and propylene carbonate -  $\text{CaCl}_2$  electrolyte.  $\text{CaCl}_2$  was chosen because the cell was used exposed to the atmosphere and  $\text{AlCl}_3$  hydrolyzes to form a scum of  $\text{Al}(\text{OH})_3$  when moist air comes in contact with the surface of the PC- $\text{AlCl}_3$  electrolyte.

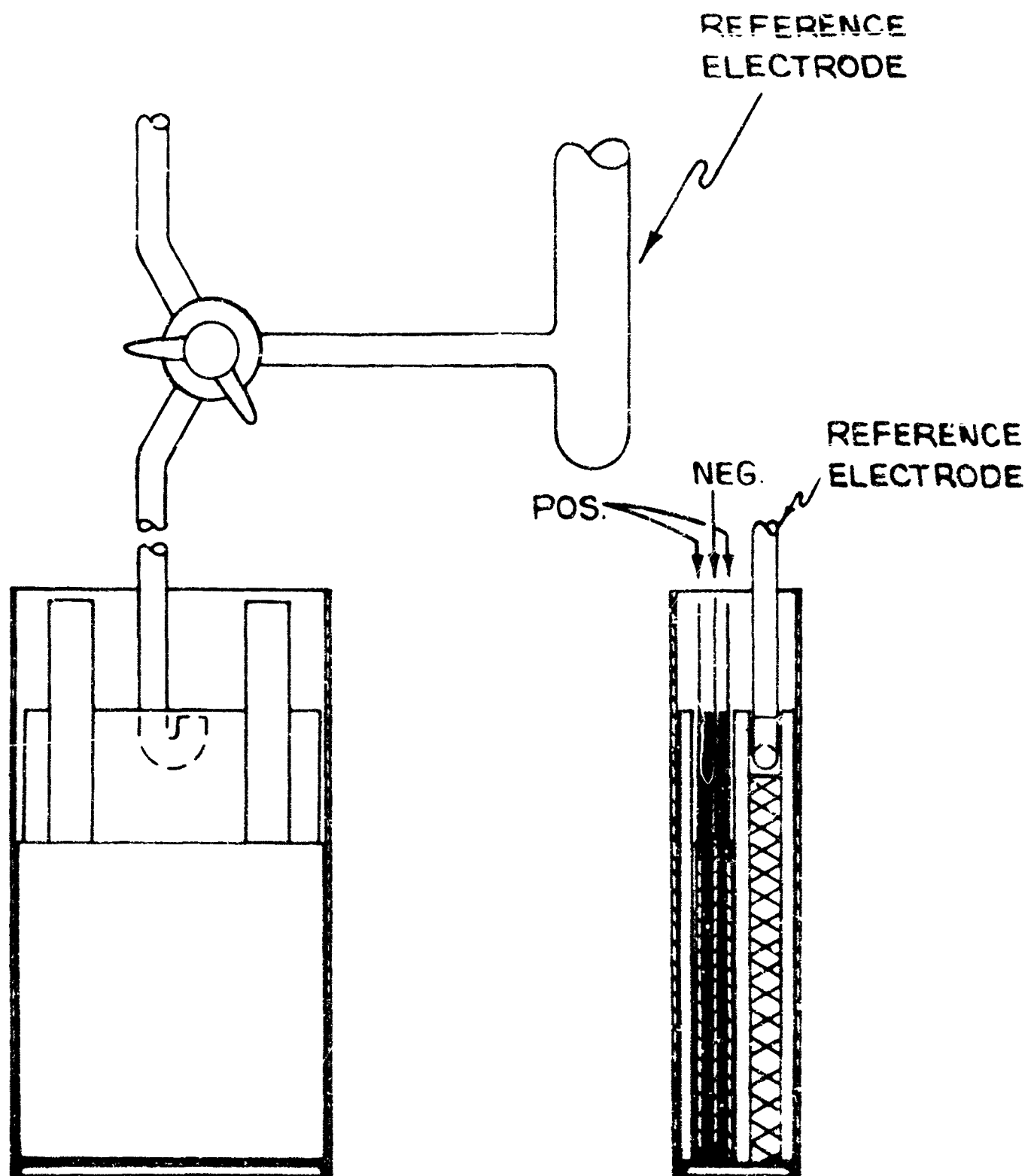


FIG. 4 EXPERIMENTAL CELL CONFIGURATION  
2 POSITIVES AND 1 NEGATIVE  
POLYPROPYLENE SEPARATOR

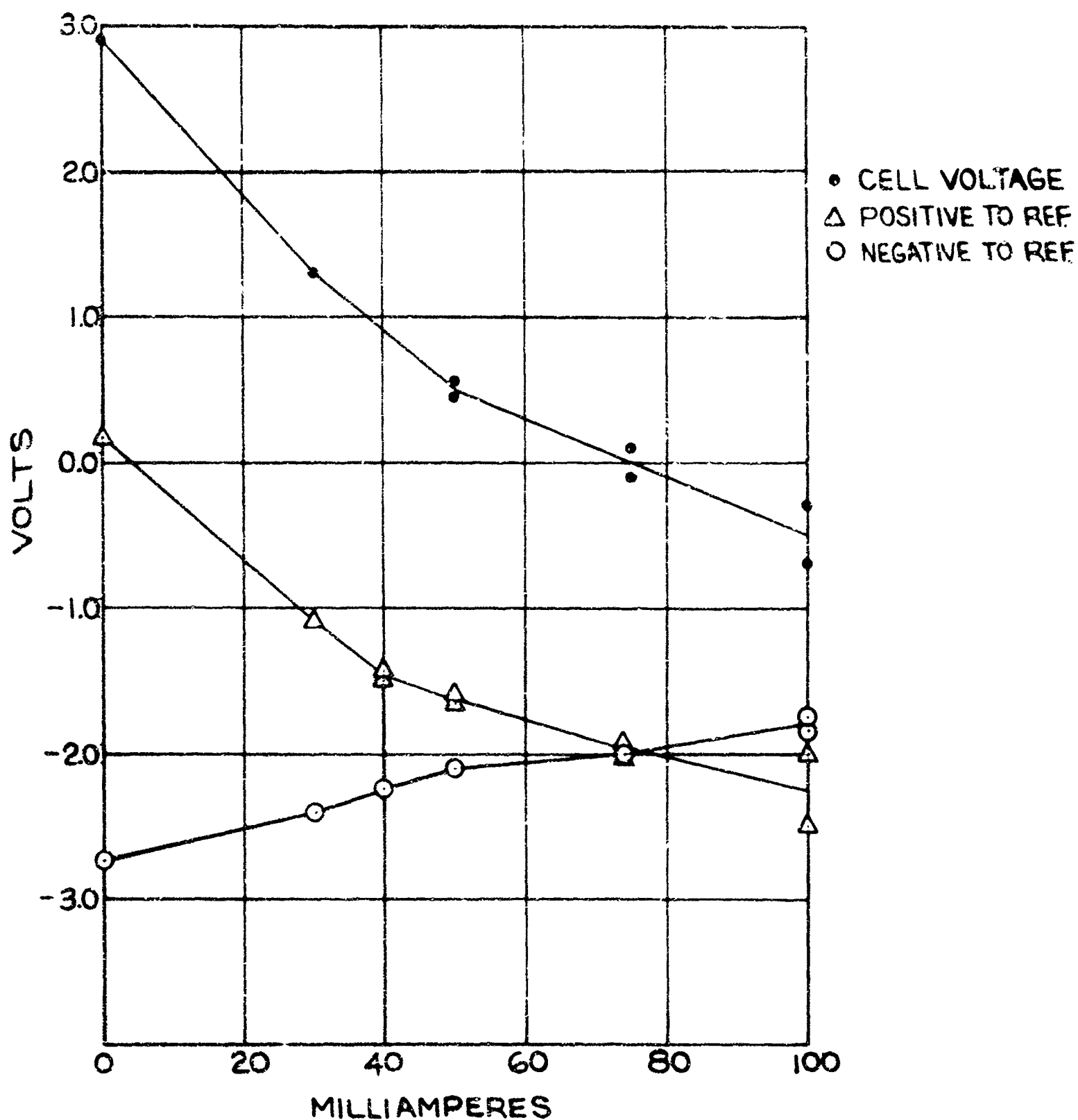


FIG. 5 NICKEL CHLORIDE-LITHIUM POLARIZATION TEST, 2 POSITIVES AND 1 NEGATIVE ELECTRODE AREA 3.05 SQ. IN. PC ELECTROLYTE WITH  $AlCl_3$

One positive electrode of a series from which previous data had been taken was formed in this way. It was charged and discharged at  $10 \text{ ma/in}^2$ . The cut-off voltage was 0.0 volt. When it was tested, it had better polarization characteristics but the utilization was increased very slightly.

The discharge capacity of a 3.0 sq. inch electrode containing a theoretical 0.93 ampere hours was only 0.017 ampere hours. This gave a 1.8% utilization when discharged at  $10 \text{ ma/in}^2$  to 1.0 volt.

As a method of overcoming the polarization, a nickel plaque was given only one impregnation. It was felt that by decreasing the amount of loading of  $\text{NiCl}_2$ , and thereby producing thinner surface films of active material, the polarization would be decreased.

The theoretical capacity of this plate was 0.17 ampere hours. The total ampere hour output of the plate was 0.06 AH at  $33.2 \text{ ma/in}^2$  to 1.0 volt, followed by  $16.6 \text{ ma/in}^2$ , again to 1.0 volt. This represents a 35% utilization, a marked improvement over the 1.8% encountered previously.

The electrodes were recharged for 0.13 AH at  $1.0 \text{ ma/in}^2$ .

The ensuing discharge with cell voltage also monitored, Figure 6, was begun at 100 ma ( $16.6 \text{ ma/in}^2$ ), but after 11 minutes the cell voltage decreased from 1.6 to 0.3 volt, and current was decreased to 50 ma ( $8.3 \text{ ma/in}^2$ ). After 65 minutes, the discharge was interrupted for one hour and then continued for an additional 55 minutes at the same c.d. It should be noted that the behavior of the cell and of the positive electrode are essentially the same.

The  $\text{NiCl}_2$  plate yielded 0.11 AH to the cut-off point which was when cell voltage reached 0.6 volt. This represents a utilization of almost 65% of the theoretical capacity. Whereas, during the initial discharge there was relatively little polarization at  $16.6 \text{ ma/in}^2$ , or even  $33.2 \text{ ma/in}^2$ , current could not be sustained for any length of time at  $16.6 \text{ ma/in}^2$  during the second discharge even though available capacity of the plate had increased.

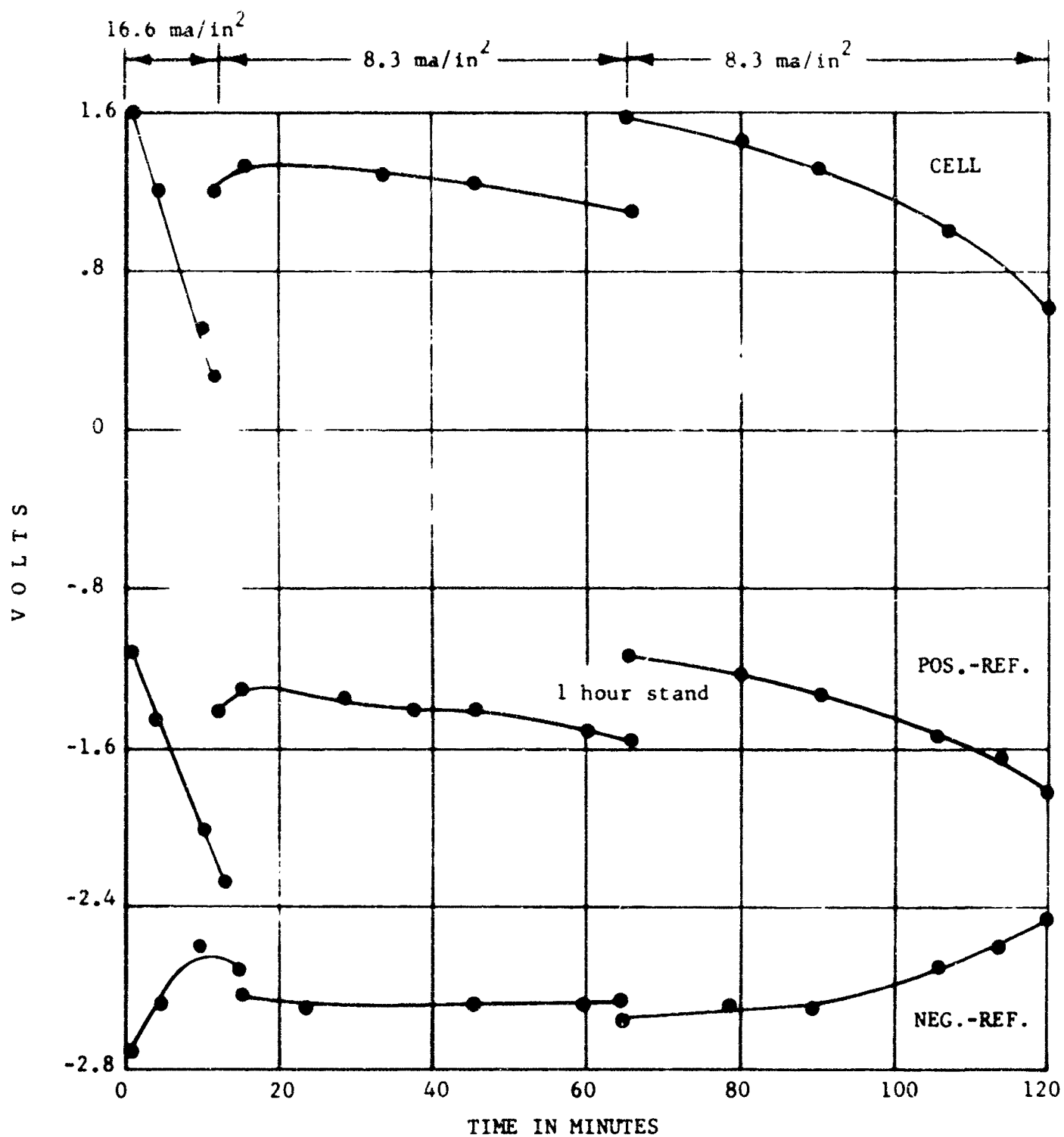


FIGURE 6 - POSITIVE ELECTRODE DISCHARGE (SECOND CYCLE)  
 $\text{NiCl}_2$  CATHODE -  $\text{Li}$  ANODE - ELECTROLYTE -  
 PROPYLENE CARBONATE -  $\text{AlCl}_3$  - CATHODE AREA  
 6 SQUARE INCHES



For some, as yet unknown reason, the electrolyte darkened during the discharge. Because of the recovery from polarization on stand, it was hypothesized that there was a concentration polarization taking place in the sintered nickel plaque. To investigate this, the apparatus in Figure 2 was used.

A fully impregnated ( $0.7 \text{ g/in}^2$ ) nickel chloride electrode was placed in the Buchner funnel. The plates were  $1\frac{1}{2}$  inch on a side. The electrolyte was propylene carbonate, with 100 grams per liter of  $\text{AlCl}_3$ , and saturated with  $\text{LiCl}$ .

The apparatus was assembled inside the glove box with a dry argon atmosphere. The valve from the vacuum pump was closed. Electrolyte was added and a small amount flowed through until the pressure in the flask was sufficient to keep any more from coming through the electrodes. Open circuit potentials were obtained. A discharge current of 20 ma was applied. After about 4 minutes the cell voltage leveled off at 1.42 volts and the positive to reference potential was -1.48 volts. The valve was opened to evacuate the flask and pull the electrolyte through the cathode pores. The positive to reference potential went more negative. Because this was not expected, the positive to reference potential was off scale and its actual value is not known. The cell voltage, however, went to 0.95 volts. Based on this, it is a good approximation to say the positive to reference potential went to -1.95 volts.

The results of this experiment did not substantiate the hypothesis of a concentration polarization, since a normal concentration polarization would have resulted in a decrease in polarization. The electrolyte had taken on a gray coloration instead of the previous straw color. A test of the conductivity indicated an increase of 10 ohms-cm from the original 90 ohm-cm. The cause of this color and conductivity change was not determined. It is

be. It is noted that the electrolyte is taking part in the reaction and is not merely acting as a conductive path for electrons.

The experiment was repeated with a new cathode from the same lot of impregnated plaques. This time the current was kept at 10 ma,  $6.4 \text{ ma/in}^2$ . The cell voltage was at 2.07 and the positive to reference was at -0.98V. When the vacuum was applied, the cell voltage again decreased, this time to 2.00 V, and the positive to reference potential went to -1.04 V. The electrolyte was recycled from the vacuum flask. This time there was no change with or without the electrolyte moving through the plaque. The cell voltage remained at 2.00 V (with slight random deviations) and the positive to reference potential was about -1.05 V.

After the first pass through the electrode, the electrolyte changed to a blue-gray color. The resistivity was again slightly greater; this time less than 10 ohms change. Because of the color change in the electrolyte, it was thought that there is some chemical reaction involved between the electrolyte and the cathode, other than a transfer of chloride ions. Tests which are discussed in Section VI - Electrolyte Studies resulted in a chlorinated form of  $\text{PC-AlCl}_3$  electrolyte. The polarization tests were repeated using this new electrolyte.

The apparatus was assembled using another cathode from the same batch as the previous tests. Figure 7 is a plot of the cell voltage (taken directly from the recorder plot) and the positive to reference potential. The latter was superimposed on the recorder plot. These reference potentials were taken with a VTVM having a 23 megohm input impedance. In this case, the cell voltage remained higher than usual during discharge at  $6.4 \text{ ma/in}^2$  and the positive to reference potential recovered from 0.04 to 0.08 volts. The current was increased to  $12.8 \text{ ma/in}^2$  and the expected polarization started. After 6 minutes the valve to the vacuum pump was opened for 15 seconds.

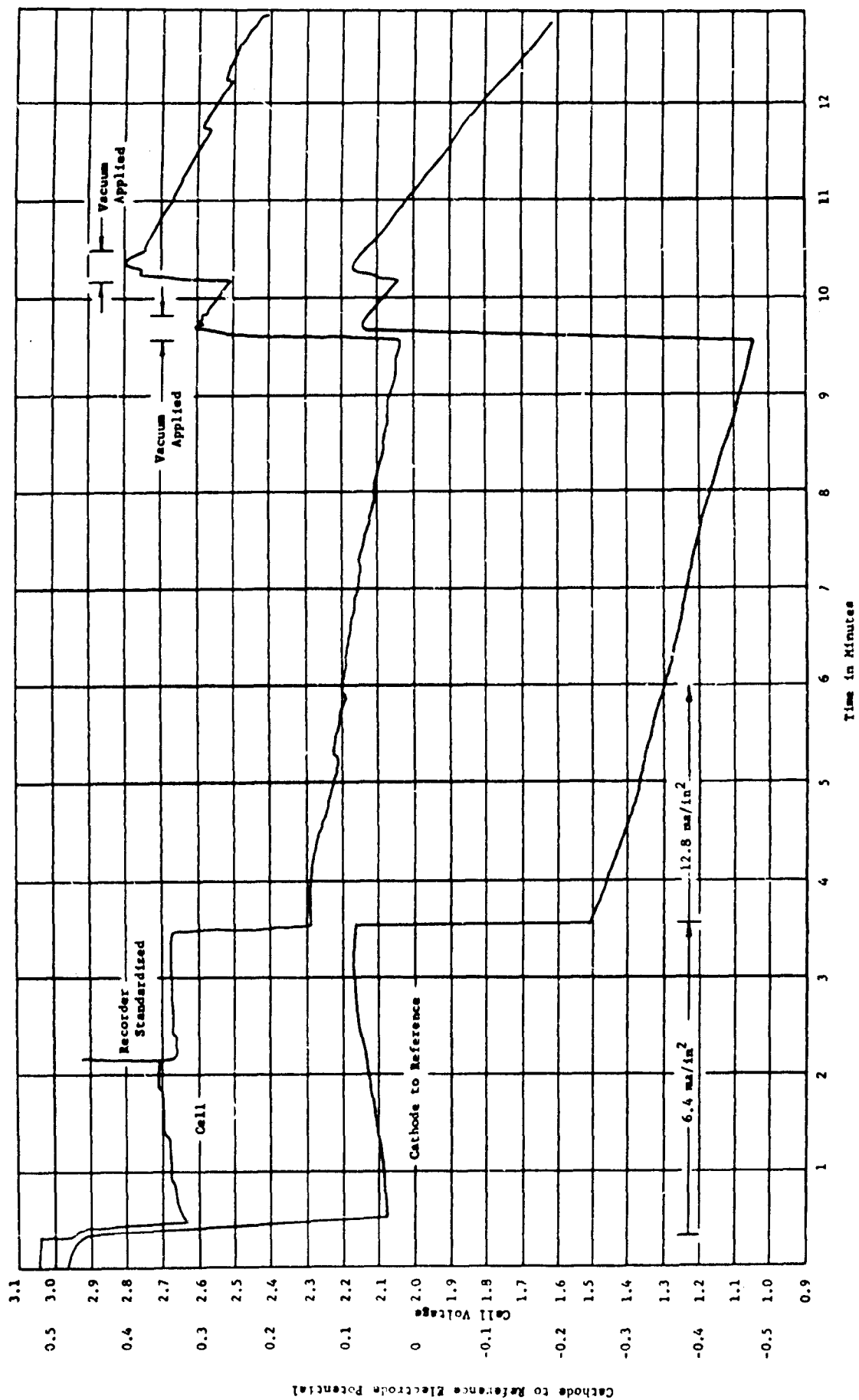


FIGURE 7 POLARIZATION TEST WITH CHLORINATED ELECTROLYTE  
 $\text{NiCl}_2$  CATHODE, PROPYLENE CARBONATE -  $\text{AlCl}_3$  ELECTROLYTE

The cell voltage increased from 2.05 to 2.60 volts. The positive to reference potential increased from  $-.048$  to  $+0.07$ . Both potentials decayed again during the 20 second period following. Again the vacuum was applied and electrolyte pulled through the pores of the cathode. This time, during the 20 second period the cell voltage increased to 2.80 volts and the positive to reference potential rose to  $+0.08$  volts. When the electrolyte ceased flowing, the voltage again decayed.

During this test, the electrolyte did not change color. Conductivity tests showed that there was no change in electrolyte resistivity.

This test indicates that there were two causes of the polarization. One may be attributed to a chlorine starved condition. In this case, rapid moving of the electrolyte through the cathode actually aggravated the situation causing a greater degree of polarization. In the case of the chlorinated electrolyte, the predominate effect was that of concentration polarization. Because of the benefits of chlorinated electrolyte, the polarization problem is significantly improved. Additional improvement in polarization will still be sought.

The first approach to further improvement in polarization was actually done earlier. This was noted when the results of partially loaded cathodes showed a decrease in polarization.

An investigation was started to determine the effect of the thickness of the sintered nickel substrate used for the cathodes. Sintered nickel material was obtained with a thickness of 17 mils, as compared with the 30 mil thick material usually used for these plaques. This material had a porosity the same as that of the 30 mil material; however, the apparent

porosity was less due to the fact that the perforated nickel substrate occupied the same volume in both cases, making the density of the 17 mil material somewhat more.

Six  $1\frac{1}{2}$  inch square plaques were made from this material and six from the standard 30 mil stock. The 12 plaques were given 4 impregnation cycles without formation. The weight gains of each plaque were checked after each impregnation. There was good grouping of weight gains in each of the thickness categories. Three plaques of the 17 mil and three of the 30 mil stock were given another 4 impregnation cycles, yielding a total of 8. These 8 impregnations loaded the 30 mil stock to approximately 0.32 grams per square inch. This is slightly less than the ratios of gain to thickness for the two materials.

These plates were then subjected to the polarization tests previously described. Each plate was given the following cycle: electrolyte was added and the cell set on open circuit for 5 minutes; the cell was discharged at  $12.8 \text{ ma/in}^2$  for 10 minutes; while keeping the current constant, a vacuum was applied to the flask and electrolyte allowed to flow through the plate at a rate of approximately 50 cc per minute. A total of 250 cc of electrolyte was used with each plate. It was found that the rate at which the electrolyte flowed through the pores was critical. Some electrolyte flowed around the edges of the cathode. Results were not repeatable to our satisfaction. The trend indicates that the thin material has a lower concentration polarization at both the partial and full loading.

### 3. Formation Cycling

Work has been progressing towards preparing positive electrodes for laboratory cells. The technique used is as follows. The sintered nickel plaques (30 mils thick and 80% porosity) are impregnated with an alcoholic solution of nickel chloride, described in Table VI. They are dried and vacuum desiccated. These plates are assembled in a beaker, along with pasted lithium plates having an excess of capacity, to make a "formation" cell. The plates are separated with perforated 1/16" polyethylene spacers. The anodes are placed in polypropylene separator bags. A false bottom made of perforated polyethylene and placed in the beaker permits a magnetic stirrer to be used to agitate the electrolyte during formation. The beaker is filled with chlorinated PC-AlCl<sub>3</sub> electrolyte and a reference electrode is used to determine the state of both anode and cathode. The entire system is kept in an inert atmosphere of argon.

The "formation" cell is discharged at a low rate (C/100 based on the theoretical capacity by weight gain) until there is a rapid change in positive to reference voltage. If the cathode does not deliver 60% of theoretical capacity, it is recharged and again discharged. Delivery in excess of 60% of theoretical capacity on the second cycle is an arbitrary requirement. Less than 60% would cause us to reject the plates, but to date, this has not been encountered.

The discharged cathodes are washed first in acetone and then in ether. They are dried and reimpregnated as before. These are again assembled in a "formation" cell. The cell is charged to the extent of the capacity removed on the previous discharge, and then discharged again. The same rule of 60% capacity delivery applies. This procedure is repeated until a theoretical capacity of 0.28 ampere hours/sq. inch for a 30 mil thick plaque is obtained.

During the charge portion of the third formation cycle, the cell voltage reached 4.8 volts, and reference potentials indicated it was due to the negative (lithium) electrode. The electrolyte had turned dark brown. A check of the anode code numbers (in the log book) showed that they were essentially fully charged. This meant that the nickel was taking chloride ions from the electrolyte. The electrolyte was chlorinated and the cell voltage dropped from 4.8 V to 3.75 V. Figure 8 is a plot of the cell voltage, and the cathode and anode to reference electrode potentials. It should be noted that the chlorination did not significantly affect the  $\text{NiCl}_2$  potential. The current was increased to  $0.5 \text{ ma/in}^2$  after 78 minutes, and both cathode and anode showed an increase in polarization. However, it was not significant, and the current was increased to  $1.0 \text{ ma/in}^2$ . The positive to reference changed little, most of the change being in the negative electrode. Figure 8 is only a portion of the total input, the  $1.0 \text{ ma/in}^2$  portion extending a total of 15.6 ampere minutes. The final positive to reference voltage was 1.63 volts. This set of 10 cathodes contained 0.5 grams per plate, corresponding to 2.0 AH. The next discharge delivered slightly over 1.6 ampere hours at  $0.4 \text{ ma/in}^2$ , yielding an 80% utilization of theoretical capacity.

During these formation cycles, there was a considerable amount of corrosion on the tabs of the nickel chloride positives. The upper photograph in Figure 1 shows the tab area of two pairs of such electrodes. There are two approaches being taken to ameliorate the situation. The first is to coat the tabs with some protective material. Several materials of known inertness are being tested for adhesion. Among these are low density polyethylene, an epoxy, and polypropylene. The polypropylene used has a flow point that is too high for easy handling. The polyethylene has a tendency to creep into the sintered plaque area during the drying of the nickel chloride. This reduces the active area of the plate. The best method so far is to coat

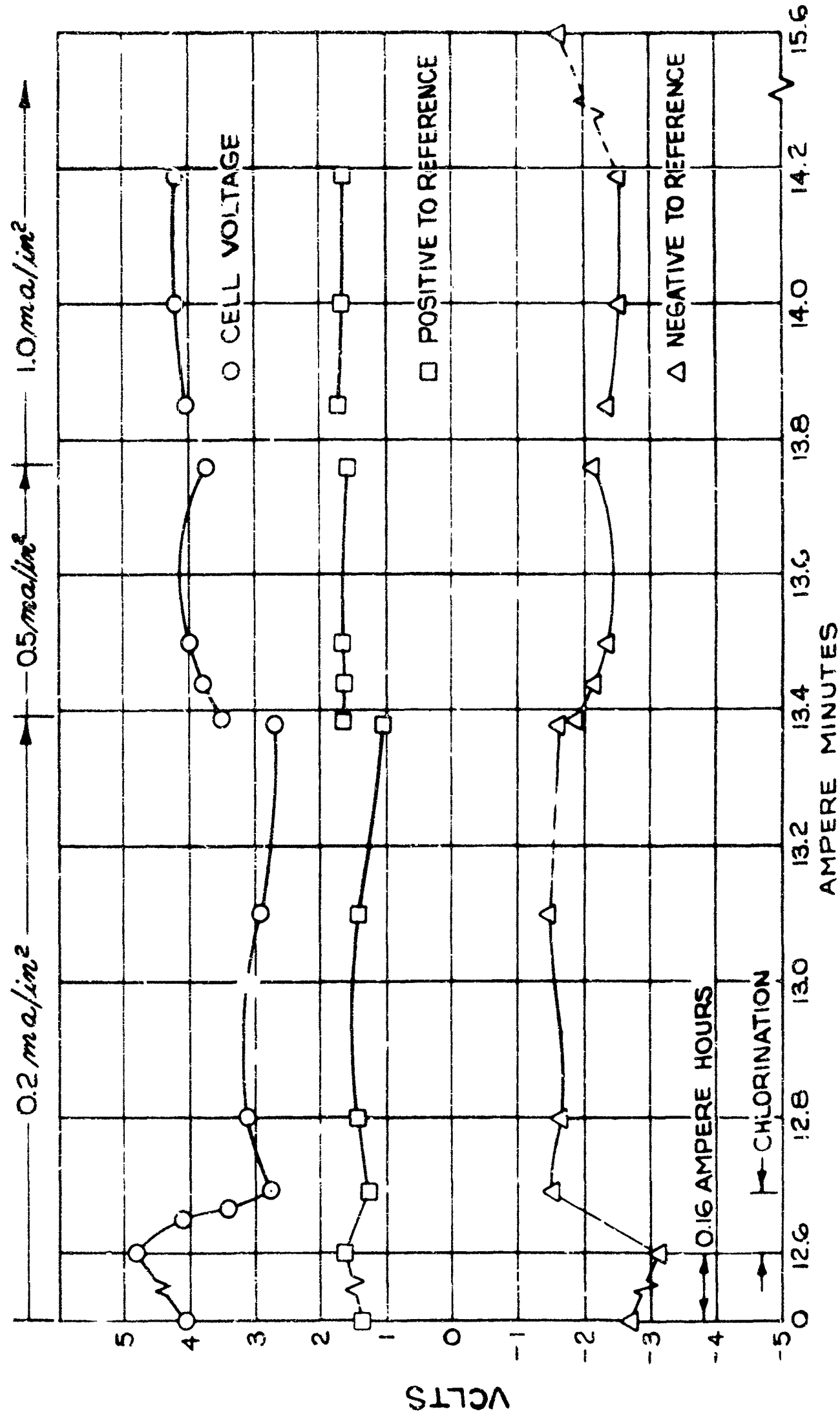


FIG. 8 FORMATION CYCLE #3 - PORTION of CHARGE



the tabs with an epoxy paint. Further investigations are being made to coat the tabs with a fluorinated ethylene-propylene co-polymer, which is inert.

The second approach is to utilize an alloy having a greater inertness than nickel. For this, tests are being conducted with Monel and Hastelloy B. This inertness is nobility, which is a resistance to electrochemical corrosion.

#### 4. Nickel Chloride - Magnesium Chloride Doped Electrodes.

A fully loaded nickel chloride cathode, containing 5% magnesium chloride doping agent, was tested in a half cell. Two lithium electrodes were used in conjunction with the  $\text{PC-AlCl}_3$  electrolyte. The discharge showed an initial polarization the same as an undoped  $\text{NiCl}_2$  electrode. However, at a low current of  $10 \text{ ma/in}^2$ , there was 7% utilization as compared with 2% of an undoped, unformed  $\text{NiCl}_2$  electrode. This is without any formation cycles.

The cell was put on charge, and the polarization was so excessive, that, at 6 volts, the current was less than  $2.0 \text{ ma/in}^2$ . Within a few minutes, the cell indicated an open circuit. After disassembly, an examination revealed that the nickel tabs on the  $\text{NiCl}_2$  electrode had been corroded away. A second tab was put on the cathode, and the cell reassembled. On charge, the same polarization occurred again, and the tab began to react to form  $\text{NiCl}_2$ . The test was stopped. This phenomenon may be enlightening from the point of what effect impurities in the cathode may have on polarization. Qualitative analysis of the electrolyte did not reveal any magnesium. Physical examination of the plate showed no unusual features.

### 5. Nickel Fluoride

The polarization of the nickel fluoride electrode on discharge was great. When short circuited through a milliamperemeter with an internal resistance of 4.5 ohms, the current fell off to  $0.64 \text{ ma/in}^2$  almost immediately. The lithium electrode showed no appreciable change. When a polarographic plot was attempted on discharge, the polarization of the nickel fluoride increased at a rapid rate even at current densities as low as  $0.1 \text{ ma/in}^2$ . No steady current-voltage relationship could be obtained. On charge, steady current readings were obtained for various current settings. Figure 9 is a plot of the steady voltage versus current density for the nickel fluoride electrodes. The values for the lithium electrodes and cell are for comparison only, and the current densities are only relative values.

Because of the high degree of polarization, no figures on utilization were obtained.

The cause of the polarization has not yet been determined. Several hypotheses have been advanced. The most favored one is that a concentration polarization is set up in the pores of the sintered nickel plaques.

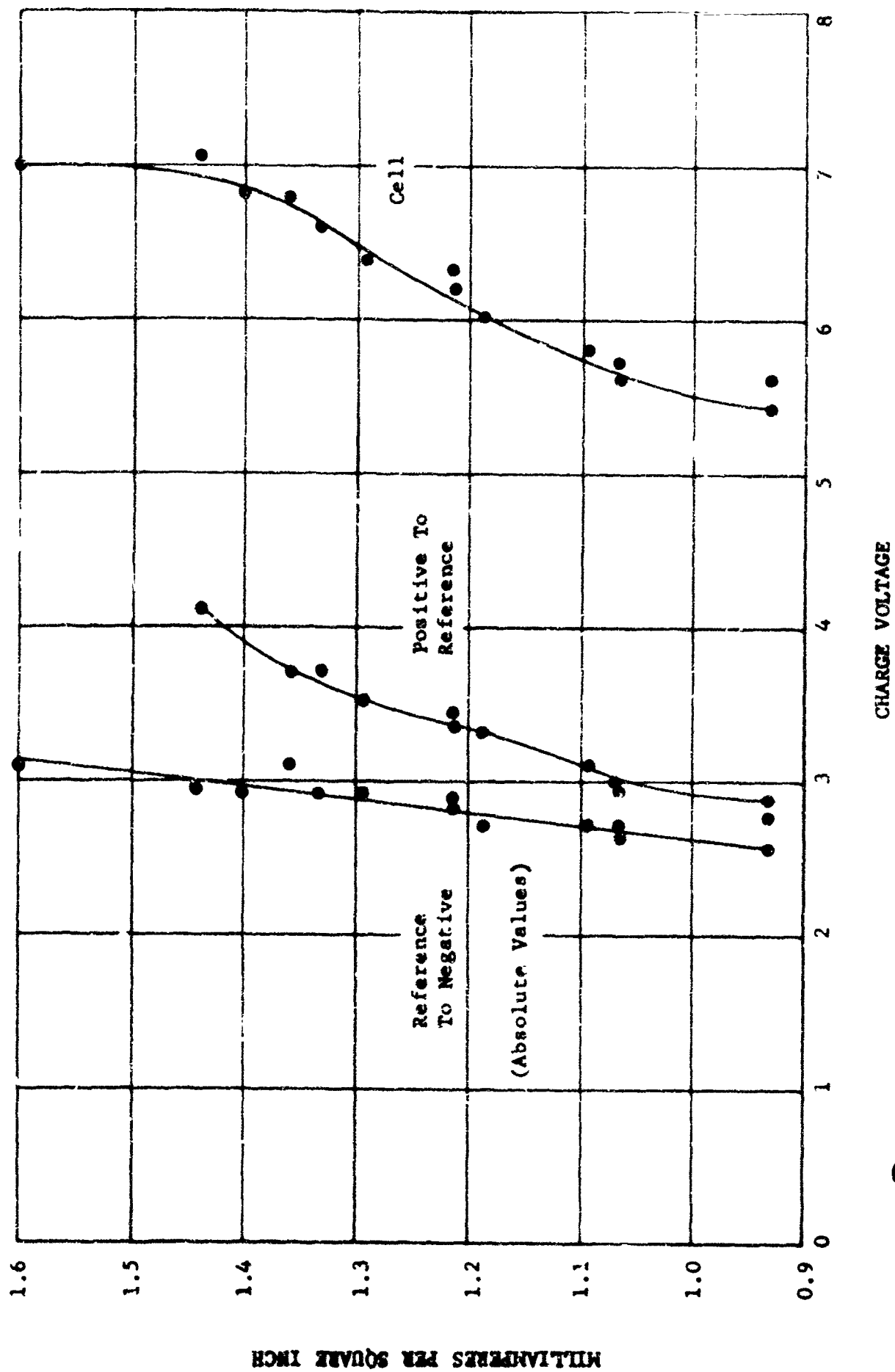


FIGURE 9

POLARIZATION STUDIES N1 F2 ELECTRODE ON CHARGE

## VI ELECTROLYTE STUDIES

### A. PROBLEM

During the course of studies concerning the positive nickel chloride electrode, the effect of darkening of the electrolyte was observed. A second important phenomenon was observed when electrolyte was drawn through a sintered nickel plaque during polarization studies. This phenomenon indicated that there was some deficiency in the electrolyte which was alleviated by permitting the nickel chloride electrode to stand for a short period of time between discharge pulses or discharging at very low rates in the region of  $2 \text{ ma/in}^2 \text{ c.d.}$

Two courses were open for endeavor. First was to find a new electrolyte. The second was to treat the electrolyte to reduce the phenomenon of interaction between the electrolyte and the nickel chloride.

### B. METHOD OF APPROACH

To determine if another electrolyte would alleviate the problem, the tables of compatibility testing and electrolyte conduction were consulted. From these tables nitromethane -  $\text{PCl}_5$  was chosen for half cell testing.

Because the chloride ion was the common denominator in the electrolyte-positive electrode system, work was centered on this point.

### C. EXPERIMENTAL RESULTS

#### 1. Nitromethane - $\text{PCl}_5$

Previous tests indicated that nitromethane containing  $13.3\text{g/L}$  of  $\text{PCl}_5$  might be a suitable electrolyte. Although compatibility tests indicate there is no effect of the proposed electrolyte on lithium or nickel chloride, the electrochemical tests indicated different results. The open

circuit potential was only 0.73 volts. The positive to reference potential was 0.22 volts. Without applying current, electrolyte was pulled through the cathode. The cell potential increased to 1.10 volts and the positive to reference potential to 0.33 volts. The reference to negative potential was 0.78 volts. A  $6.4 \text{ ma/in}^2$  current was applied while the electrolyte was flowing and both the positive and the negative electrodes reversed. No further tests have been conducted on this electrolyte.

## 2. Propylene Carbonate - $\text{AlCl}_3$

Several attempts had been made to purify the aluminum chloride for the electrolyte. To date, the best technique has been to hand select the purest looking (white, free from discoloration) granules from a reagent grade material. There is a large amount of dark colored material in the purest available aluminum chloride. Even using select material, the electrolyte becomes dark in color on standing.

A sample of propylene carbonate containing 100 grams per liter of aluminum chloride was made up. It stood in a tightly closed bottle for a week, during which time it became dark brown. The sample was divided into two parts and chlorine gas bubbled through half of it. Within minutes the color returned to the original straw yellow. A piece of lithium wire was placed in the chlorinated portion and again sealed. After a day the conductivities of the original and the chlorinated sample were checked. The ohmic values were the same, but the capacitive portion of the chlorinated sample was greater. This could be the result of a change in the dielectric constant of the electrolyte. The color of the chlorinated sample was still light straw.

The electrolyte was analyzed for chlorine before and after chlorination. This was done after reacting with lithium wire. Before

chlorination the chloride ion content was 65.7g/L and after chlorination it increased to 78.1g/L. Based on 100g/L of  $\text{AlCl}_3$  the chloride ion content should have been 79.8g/L. The expected value is even greater because there is some lithium chloride dissolved in the material. At present we have no explanation for the difference.

Previous electrolytes were prepared from lumps of fused anhydrous  $\text{AlCl}_3$ . The material now used is a sublimed powder. It was observed that when the powder found in with the lumps of fused material was used, a brown color appeared in the electrolyte. The lumps very seldom produced this effect. This brown color did not necessarily form when the  $\text{AlCl}_3$  was added but sometimes occurred several hours later. There was some darkening with time for the lump material too, but to a lesser degree. When the anhydrous sublimed powder was used, the brown color appeared with the evolution of heat. When the powder was added by dusting the surface, instead of dumping it in, the brown color did not appear. Again there was some darkening, but to a lesser degree. There was also less heat involved. After the solution was saturated with aluminum chloride, the rate or manner in which more was added did not matter. The technique now used is to add the  $\text{AlCl}_3$  to a small amount of PC to saturate it. Then a large amount of excess  $\text{AlCl}_3$  added. Finally, more PC is added to bring the concentration to 100 grams per liter. The solution is then chlorinated and stored with a piece of lithium wire in it to scavenge the excess chlorine. This technique starts with a lighter colored material than that produced by rapid addition of  $\text{AlCl}_3$ , and the chlorination lightens the color to produce a final product of a pale yellow color compared to the usual straw color.

In order to determine whether the darkening in color is due to local heating during the dissolving of the  $\text{AlCl}_3$ , some samples

of electrolyte were made by carefully dusting the  $\text{AlCl}_3$  into the propylene carbonate. These were heated to various temperatures. The colors changed from a straw color to dark brown, almost black. This could be achieved either through moderate heating for a prolonged time or rapid heating at a high temperature. Samples were taken at various color points from light brown to the almost black. These were then chlorinated. The light to medium brown samples returned to the straw color, but the darker samples did not. Even when a dark sample was diluted with fresh PC and chlorinated, the color did not return to the straw. Infra red analyses have not been made to determine what the dark color is caused by.

A sample of propylene carbonate was chlorinated first, and then the  $\text{AlCl}_3$  added. In this case there was no discoloration regardless of the rate of addition of the  $\text{AlCl}_3$ . Samples treated this way and scavenged with lithium have the same properties as the regular chlorinated sample. The electrolyte does not seem to heat up much during the addition of  $\text{AlCl}_3$  after it has been chlorinated.

A similar experiment was tried with water and  $\text{AlCl}_3$ . A portion of powdered  $\text{AlCl}_3$  was added to water in a test tube. The solution became so hot the test tube could not be hand held. An equal amount of water in another test tube was chlorinated and again  $\text{AlCl}_3$  added. In this case the solution became warm but not hot.

There is no apparent reason why the chlorination should reduce the color. The effect of heating does not parallel the effect of a chloride deficiency reported in the section on Formation Cycling. A hypothesis is that when there is a deficiency of available chloride ions there is local heating. The so-called "Anode Effect" observed in electrochemical refining is a similar situation.

## VII CONCLUSIONS AND RECOMMENDATIONS

There have been several important accomplishments made during the year, not the least of which has been the reduction of the problem to one of eliminating polarization of the positive nickel chloride electrode. Discharge rates approximating the 40 hour rate have been achieved. Good utilization and reversibility of the system have also been realized at these low rates. The factor limiting discharge to low rate appears to be excessive concentration polarization of the nickel chloride electrode.

The negative, or lithium electrode, has been stabilized. However, for extended cycle life, further improvement may be necessary. Under the limited cycling involved during formation of the positive electrodes, there is good indication that the lithium electrode improves with use, providing impurities are excluded from the system. This is most noticeable during formation cycling when the cells are being assembled and disassembled.

Of the many separators investigated, three have been used in flooded cells, each with about the same degree of success. These are a non-woven polypropylene, a Teflon-fiberglass paper, and an asbestos-fiberglass paper. The degree of electrolyte absorption and retention of the polypropylene and the asbestos-fiberglass paper is superior to that of the Teflon-fiberglass. This property would be an essential one if a limited amount of electrolyte were to be used. All three materials have been used in formation cycling of electrodes and polarization studies.

For the chloride system there are two usable electrolytes. The best of these two is propylene carbonate -  $\text{AlCl}_3$ . The present form of chlorinated propylene carbonate, containing 0.75 M  $\text{AlCl}_3$  and saturated with lithium chloride, has overcome one form of polarization to which the system



was susceptible. To what degree the electrolyte contributes to the concentration polarization should be determined.

The second electrolyte is the nitromethane -  $\text{AlCl}_3$  electrolyte. Since the discharged state of the negative electrode is  $\text{LiCl}$ , the electrolyte must be saturated with it. The nitromethane -  $\text{AlCl}_3$  electrolyte decreases in conductivity when  $\text{LiCl}$  is added. The resulting conductivity makes this electrolyte less desirable than the propylene carbonate.

The two most satisfactory electrolytes, of those evaluated in this program for the fluoride system, are N-methyl-2-pyrrolidone and dimethylsulfoxide, both with zinc fluoride. Neither of these electrolytes show the degree of conductivity found in the chloride system. Both are about one order of magnitude lower than propylene carbonate -  $\text{AlCl}_3$ . Neither is affected by the addition of  $\text{LiF}$ . This is in marked difference to the two chloride electrolytes which are affected by  $\text{LiCl}$ .

The problems encountered with the polarization of the positive electrode have been, and remain, the most difficult to overcome. Much progress has been made in the degree of utilization of the active material. The technique of "formation cycling" between impregnations of  $\text{NiCl}_2$  have resulted in approximately 80% utilization of the theoretical capacity. Several active investigations are being carried out to reduce concentration polarization. The use of thinner sintered nickel plaques for the positive electrode matrix have shown some degree of improvement. Since this work is still in the preliminary stages, the results are too limited for interpretation, and it is recommended that this be continued.

The most logical endeavor now, and therefore recommended, is to determine the cause of concentration polarization. Studies to determine

the role of the electrolyte in this phenomenon must be made. Determinations of transference numbers for the electrolytes should be made. Although the present electrolyte of propylene carbonate - 0.75 M  $\text{AlCl}_3$  ( $\text{Cl}_2$ ) is the most favorable for conductivity, there may be a concentration which reduces concentration polarization without affecting the conductivity too greatly.

An impregnated sintered nickel plaque is presently being used for the positive electrode. Future experiments with pasted  $\text{NiCl}_2$  electrodes and electroformed  $\text{NiCl}_2$  on nickel sheets are recommended. With a pasted  $\text{NiCl}_2$  electrode, it may be easier to control the degree of entrapped chloride ions on discharge, than with the sintered nickel plaque. An electroformed  $\text{NiCl}_2$  on a solid substrate would eliminate the problem of entrapment in the pores of the plaque. It may, however, be impractical from the standpoint of ampere hour capacity. It will be primarily a tool for investigation.

It is believed that in solving the polarization problems of the nickel chloride electrode, a similar approach to the nickel fluoride electrode will permit further active investigation into this system. There is still an active desire to pursue the system offering a theoretically higher watt-hour per pound ration, and this must, therefore, be recommended.

The present state of the art permits the assembly of a nickel chloride-lithium cell capable of delivering approximately 80% of the theoretical capacity (based on the  $\text{NiCl}_2$  electrode) at currents approximating the C/40 rate. The charging characteristics are such that a C/20 charge rate can be used. It is believed that through an intensive effort to solve the problem of concentration polarization, the rates can be brought into line with the goals of the program. The goals specify that the battery should

should be capable of being discharged at 1.275 C rate to 75% of the rated capacity while maintaining the voltage at 27.5 volts  $\pm$  1.5 volts. It should also be capable of being recharged in 55 minutes of accepting a 0.82 C rate charge (or greater) for that period of time.